

## HIGH RESOLUTION FAR INFRARED LABORATORY SPECTROSCOPY OF TRANSIENT SPECIES: APPLICATION TO THE SO RADICAL ( $X^3\Sigma$ )

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**Abstract.** Both emission and absorption techniques have been developed at the AILES beamline of SOLEIL synchrotron to record far-infrared (FIR) spectra of transient species. To illustrate the possibilities offered by our absorption set-up, we report in this paper new rotational transitions of the SO radical falling in the spectral range covered by the HIFI spectrometer onboard Herschel.

### 1 Introduction

The far-infrared (FIR) spectral range is now explored by the space mission Herschel, which, in particular, performs high-resolution spectroscopy thanks to the HIFI heterodyne spectrometer (De Grauw *et al.* 2010). In order to complete far-infrared (FIR) line lists of transient species that are important for the astrophysical community, we have developed two discharge experiments (one for emission and one for absorption spectroscopy) at the AILES beamline of SOLEIL synchrotron facility (Roy *et al.* 2006). These experiments make use of a high resolution ( $R = 0.001 \text{ cm}^{-1}$ ) Bruker IFS 125 Fourier transform interferometer and are now opened to external users community. We report here the investigation of the SO rotational spectrum ( $X^3\Sigma$ ), a well-known interstellar radical (Gottlieb & Ball 1973).

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## 2 Experimental methods and results

Both emission and absorption discharge set-ups have been described in details elsewhere (Martin-Drumel *et al.* 2011).

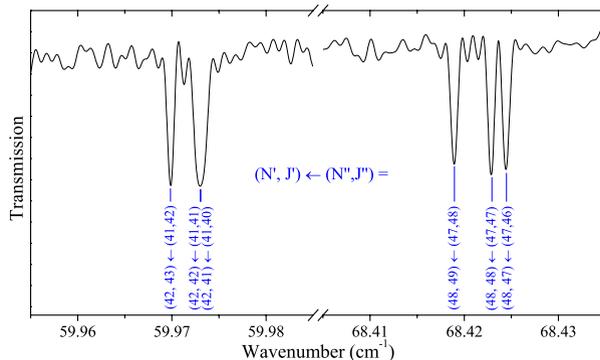
### 2.1 Emission spectroscopy of excited molecules

Despite intrinsic physical limitations in the FIR (cubic frequency dependence of the Einstein spontaneous emission coefficient and emission of the 300 K blackbody radiation), emission spectroscopy is an efficient technique to observe pure rotational transitions of excited molecules and radicals (Bernath 2000). Our emission set-up makes use of a 1000 W power radiofrequency generator (Pirali & Vervloet 2006). Vapour molecules are flowing in the excitation cell at a pressure of about 10 mbar. The resulting emission is collected by a single off-axis parabolic mirror and focused onto the entrance iris of the interferometer. Due to signal-to-noise (S/N) ratio, temperature and pressure broadenings, the resolution is limited to about 120 MHz ( $\sim 0.004 \text{ cm}^{-1}$ ) resulting in a 12 MHz accuracy on line position for the most intense transitions. Spectra of molecules and radicals excited at high rotational and vibrational temperatures (up to 2000 K) can be recorded using this technique allowing the observation of pure rotational and ro-vibrational transitions within the ground and vibrationally excited states. The experimental datasets on well-known interstellar molecules (also expected to be present in newly discovered exoplanets)  $\text{H}_2\text{O}$  (Coudert *et al.* 2004; Yu *et al.* 2012), HCN,  $\text{NH}_3$  (Yu *et al.* 2010) and radicals OH (Martin-Drumel *et al.* 2011) and  $\text{NH}_2$  have thus been completed to excited energy levels.

### 2.2 Absorption spectroscopy of radicals: FIR absorption spectrum of SO

Absorption spectroscopy, usually limited in the FIR by the low emittance of continuum sources, benefits at AILES from the high brilliance of the synchrotron radiation providing a large improvement in sensitivity. We recently developed a multipass absorption cell (24 m) equipped with two electrodes in order to record absorption spectra of radicals synthesized in the positive column of a continuous DC discharge. The improved sensitivity resulting from the relatively long path length of the cell and the synchrotron radiation source allows the use of the highest resolution of the interferometer ( $30 \text{ MHz} / 0.001 \text{ cm}^{-1}$ ) providing a line position accuracy better than 3 MHz ( $\sim 0.0001 \text{ cm}^{-1}$ ) for the strongest transitions. Spectra of several radicals have been recorded from the Mid-IR to the FIR: OH (Martin-Drumel *et al.* 2011), NH,  $^{15}\text{NH}$  (Bailleux *et al.* 2011), CH (Martin-Drumel *et al.* 2011), CN, SH, SO,  $\text{NH}_2$ ,  $^{15}\text{NH}_2$  and  $\text{C}_3$ .

The pure rotational spectrum of SO in its ground state has been extensively studied in the laboratory from the sub-millimeter to THz wavelength – see Bogey *et al.* (1997) and refs therein. However, to the best of our knowledge, no FIR broadband investigation of this radical has been reported up to date, and several rotational transitions belonging to HIFI spectral windows remain unobserved in the laboratory. We report here the first FIR observation of several rotational lines



**Fig. 1.** Part of the absorption spectrum (presented in transmission) of the SO radical.

**Table 1.** Molecular constants in MHz of the SO radical in the  $\nu = 0$  of the  $X^3\Sigma$  state and comparison to previous publications.

	This Work	CDMS 2001	Cazzoli <i>et al.</i> (1994)
$B$	21 523.556 16 (37)	21 523.555 78 (45)	21 523.554 4 (11)
$D \times 10^3$	33.915 56 (70)	33.914 3 (11)	33.913 8 (43)
$H \times 10^9$	-7.09 (17)	-7.96 (83)	-7.9 (15)
$\lambda_0$	158 254.387 (13)	158 254.387 (13)	158 254.401 (16)
$\lambda_1$	0.306 53 (20)	0.306 58 (21)	0.305 87 (66)
$\gamma_0$	-168.304 1 (40)	-168.305 2 (37)	-168.310 5 (51)
$\gamma_1 \times 10^3$	-0.523 1 (85)	-0.522 1 (87)	-0.536 (29)
Fitted lines	184	66	53
$\sigma_{fit}$ – MW (MHz)	0.264	0.1453	0.377
$\sigma_{fit}$ – FIR ( $\text{cm}^{-1}$ )	0.00005	–	–
RMS	0.64	0.65	–

of SO in the spectral range 44–93  $\text{cm}^{-1}$  at a resolution of 0.001  $\text{cm}^{-1}$  allowing an accuracy on line position of 0.00007  $\text{cm}^{-1}$  ( $\sim 2$  MHz). A continuous electrical discharge (1 A / 980 V) in a flowing mixture of  $\text{H}_2\text{S}$ , He,  $\text{H}_2$  and air (respectively 0.01, 1.15, 0.14 and 0.06 mbar) was used to produce SO (no temperature or pressure broadenings were observed in these experimental conditions). Together with lines of SO, lines of the SH radical have been identified on the resulting spectrum. Their analysis will be the subject of a future publication. Spectral calibrations were performed using residual water lines frequencies (Matsushima *et al.* 1995).

On our spectrum, 102 transitions of SO have been identified ( $N = 31$  to 65) with S/N ratio of about 5 for the most intense lines (see Fig. 1). Among the observed lines, 99 are detected for the first time (22 new transitions belong to the HIFI spectral windows). Due to our limited instrumental resolution, transitions involving  $N$  ranging from 31 to 43 show unresolved rotational triplets (see Fig. 1). Uncertainty on line position of unresolved and weak transitions has been degraded by a factor of two. The complete linelist can be provided by contacting the authors.

These transitions have been fitted together with available previously reported transitions of SO in its vibrational ground state using the SPFIT program (Pickett 1991). All the transitions included in the fitting procedure are weighted to the inverse of their accuracy squared. A total of 184 transitions have been fitted using 7 parameters of a  $^3\Sigma$  effective Hamiltonian:  $B$ ,  $\gamma_0$ ,  $\lambda_0$  – the rotational, spin-rotation interaction, spin-spin interaction constants – and their higher order terms  $D$ ,  $H$ ,  $\gamma_1$ ,  $\lambda_1$ . Table 1 summarizes the parameters derived from this work. They are in very good agreement with previous values (Cazzoli *et al.* 1994; CDMS 2001) and centrifugal distortion parameters are better determined thanks to the observation of transitions involving high rotation quantum numbers. Improving the parameter determination permits to predict more accurate energy levels and line positions to support astrophysical observations of this radical. The reduced standard deviation of the fit is 0.64.

### 3 Conclusion

The first results obtained with our two discharge set-ups demonstrate their ability to provide more complete FIR line lists on transient species to the astrophysical community. These experimental set-ups are now opened to external users by standard request for beamtime allocation<sup>1</sup>.

### References

- Bailleux, S., Martin-Drumel, M.A., Margulès, L., *et al.*, 2011, A&A, 538, A135  
Bernath, P.F., 2000, Annu. Rep. Prog. Chem. C, 96, 177  
Bogey, M., Civis, S., Delcroix, B., *et al.*, 1997, J. Mol. Spectrosc., 182, 85  
Cazzoli, G., Cludi, L., Cotti, G., Esposti, C.D., & Dore, L., 1994, J. Mol. Spectrosc., 167, 468  
CDMS, The Cologne Database for Molecular Spectroscopy, 2001, <http://www.astro.uni-koeln.de/site/vorhersagen/catalog/archive/SO/>  
Coudert, L.H., Pirali, O., Vervloet, M., Lanquetin, R., & Camy-Peyret, C., 2004, J. Mol. Spectrosc., 228, 471  
De Grauw, Th., Helmich, F.P., Philipps, T.G., *et al.*, 2010, A&A, 518, L6  
Gottlieb, C.A., & Ball, J.A., 1973, ApJ, 184, L59  
Matsushima, F., Odashima, H., Iwasaki, T., Tsunekawa, S., & Takagi, K., 1995, J. Mol. Struct., 352, 371  
Martin-Drumel, M.A., Pirali, O., Balcon, D., *et al.*, 2011, Rev. Sci. Instr., 82, 113106  
Pickett, H.M., 1991, J. Mol. Spectrosc., 148, 371  
Pirali, O., & Vervloet, M., 2006, Chem. Phys. Lett., 423, 376  
Roy, P., Rouzières, M., Qi, Z., & Chubar, O., 2006, Infrared Phys. Tech., 49, 139  
Yu, S., Pearson, J.C., Drouin, B.J., *et al.*, 2010, J. Chem. Phys., 133, 174317  
Yu, S., Pearson, J.C., Drouin, B.J., *et al.*, 2012, J. Mol. Spectrosc., in press

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